

Solubility of Nitrous Oxide in Triethylene Glycol Monomethyl Ether at Elevated Pressures

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The solubility of N_2O in a physical solvent, triethylene glycol monomethyl ether (TEGMME), has been measured at 40, 70, and 100 °C at pressures up to 10.9 MPa. The experimental results were correlated by the Peng-Robinson equation of state, and the interaction parameters and the Henry's constants were obtained. The results are compared with the solubility of N_2O in water and the solubility of CO_2 in TEGMME and water.

Introduction

Triethylene glycol monomethyl ether (TEGMME) is a physical solvent which has a strong affinity for CO_2 (Henni and Mather, 1995). TEGMME can be used alone or in an admixture with a chemical solvent such as an alkanolamine solution for the removal of acid gases from gas mixtures. Zawacki et al. (1981) listed the 26 most promising solvents for their potential of removing acidic gases from gas streams. The dimethyl ether of tetraethylene glycol (DMETEG) and *N*-formylmorpholine (NFM) topped the list. TEGMME belongs to the same chemical family as the dimethyl ether of tetraethylene glycol, but it costs 4 times less than the dimethyl ether of tetraethylene glycol and 8 times less than NFM. The solubility of nitrous oxide in the physical solvent is of interest from both the theoretical and practical points of view. N_2O has recently become the subject of intense research and debate because of its ability to deplete the ozone layer. It absorbs strongly in the infrared, contributes to the greenhouse effect, and participates in acid-rain formation. The current rate of accumulation of N_2O in the atmosphere is about 0.2–0.3% per year (Badr and Probert, 1993).

Another reason for studying the solubility of N_2O is the " N_2O analogy". For most physical and chemical mixed solvents, due to the chemical reaction that occurs, it is impossible to obtain the solubility of CO_2 in the solution in a direct way. N_2O is often used as a nonreacting gas to estimate the properties of CO_2 in view of its similar configuration, molecular volume, and electronic structure.

To the best of our knowledge, there is no study of the solubility of N_2O at other than atmospheric pressure for physical solvents commonly used in acid gas removal.

Experimental Section

The apparatus used in this work is similar to that employed by Jou et al. (1982). The windowed equilibrium cell was placed in a constant temperature bath. The temperature was controlled by a Hallikainen Thermostat within ± 0.1 °C. A 250 cm^3 tubular reservoir was mounted at the top of the cell to increase the volume of the vapor phase. The pressure in the cell was measured by a 0–13790 kPa (2000 psi) Heise gauge (Newtown, CT) with an accuracy of $\pm 0.1\%$ of the full-scale span. The temperature was measured by a calibrated iron–constantan thermocouple. The solvent was fed by gravity to the cell and heated to 120 °C. Nitrous oxide was added to an

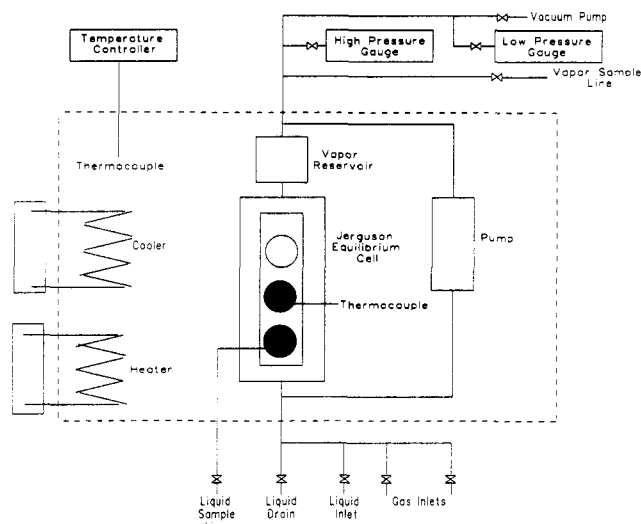


Figure 1. Schematic diagram of the experimental apparatus.

amount determined by the pressure. The vapor phase was recirculated to the bottom of the cell by a magnetic pump for about 8 h. The pump was stopped, and a sample, 2–5 g, depending on the solubility, was withdrawn into a 50 cm^3 sample bomb which had previously been evacuated and weighed. The bomb was reweighed to obtain the mass of the sample and attached to a 100 cm^3 buret. A magnetic stirring bar was contained in the bomb to assist in the degassing process. The valve on the bomb was opened, and the nitrous oxide evolved from the liquid sample was collected over mercury in the buret. The mass of nitrous oxide evolved was calculated using atmospheric pressure, room temperature, and the volume collected. The solubility at low pressures and the residual nitrous oxide at atmospheric pressure were measured by gas chromatography. A 5- μ L sample followed by a 20- μ L sample of nitrous oxide was injected into the gas chromatograph (Hewlett-Packard 5710A, Avondale, PA) equipped with a thermal conductivity detector and containing a column, 3 m long with 6.35 mm o.d., packed with Chromosorb 104. The column was operated at a temperature of 25 °C and programmed to reach 250 °C after the appearance of the nitrous oxide peak. The vapor sample was sent directly to the gas chromatograph. No TEGMME could be detected in the vapor phase. Helium was used as a carrier gas with a flow rate of 22 mL/min. Figure 1 is a schematic diagram of the equipment for the solubility measurements. TEGMME with a purity of 95 mass % (2% each of diethylene and tetraethylene

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Table 1. Solubility of Nitrous Oxide (2) in TEGMME (1)

40 °C		70 °C		100 °C	
P^a/kPa	x_2^b	P/kPa	x_2	P/kPa	x_2
356	0.035	315	0.036	535	0.045
439	0.060	577	0.047	879	0.060
839	0.116	783	0.070	2286	0.129
1146	0.153	1060	0.114	3128	0.171
2135	0.215	1750	0.150	3651	0.204
2783	0.272	2396	0.201	4328	0.247
3610	0.317	3859	0.248	5183	0.264
4231	0.371	4603	0.312	5376	0.271
4894	0.415	5306	0.341	6437	0.306
6023	0.531	5954	0.394	7431	0.340
7431	0.546	6739	0.442	8781	0.375
		8021	0.455	9813	0.405
		9540	0.502	10889	0.448
		10395	0.512		

^a Total pressure. ^b Mole fraction in the liquid phase.

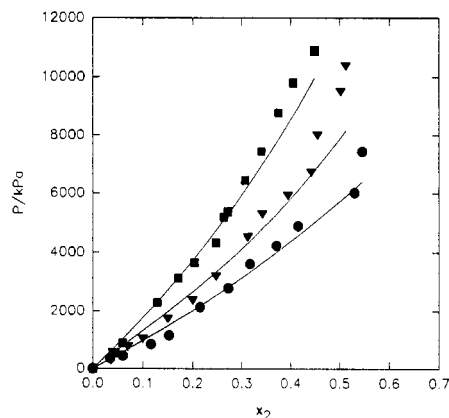


Figure 2. Solubility of nitrous oxide in TEGMME: ●, 40 °C; ▼, 70 °C, ■, 100 °C; —, Peng–Robinson correlation.

Table 2. Pure Component Parameters for the Peng–Robinson Equation of State

compound	T_c/K	P_c/kPa	ω
N ₂ O ^a	309.6	7345	0.142
CO ₂ ^b	304.2	7381	0.225
TEGMME ^c	682.4	4880	1.119

^a From Daubert and Danner (1991). ^b From Angus et al. (1976). ^c From Henni and Mather (1995).

glycol ethers) was purchased from Aldrich Chemical Co. (Milwaukee, WI). Nitrous oxide was supplied by Linde (Edmonton, Alberta, Canada) and was specified to be 99+ vol % pure. Duplicate analyses agreed within ± 0.002 mole fraction.

Results and Discussion

The solubility data of N₂O in TEGMME at 40, 70, and 100 °C are presented in Table 1. The solubility data were correlated using the Peng–Robinson (1976) equation of state and presented in Figure 2. The critical pressure (P_c) and critical temperature (T_c) for TEGMME were estimated using the correlation of Lydersen (Reid et al., 1987). The acentric factor (ω) was obtained from the Lee–Kesler correlation (Reid et al., 1987). The constants in the Antoine equation were published by Troch et al. (1991). The parameters for pure N₂O were published by Daubert and Danner (1991). These parameters are presented in Table 2.

The interaction parameter in the mixing rule of the equation of state was obtained in a stepwise fashion by minimizing the error in the predicted bubble point pressure using the following objective function:

Table 3. Peng–Robinson Interaction Parameters for the N₂O (2) + TEGMME (1) System

T/K	δ_{12}	$f/\%$
313.2	0.048	13.0
343.2	0.030	12.7
373.2	0.041	9.3

Table 4. A Comparison of the Henry's Constants for Nitrous Oxide and Carbon Dioxide in TEGMME and Water

T/K	Henry's constant/MPa		ratio ^b in TEGMME	ratio ^c in water
	N ₂ O	CO ₂ ^a		
313.2	8.10	7.50	1.08	1.41
343.2	9.31	8.39	1.11	1.42
373.2	12.90	11.84	1.09	1.41

^a From Henni and Mather (1995). ^b $H_{N_2O-TEGMME}/H_{CO_2-TEGMME}$. ^c From Jou et al. (1992).

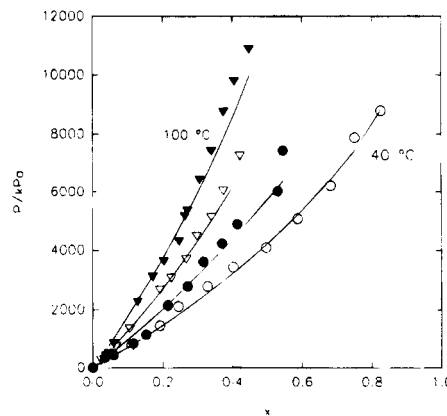


Figure 3. Mole fraction solubility x of nitrous oxide and carbon dioxide in TEGMME: ○, ▼, CO₂; ●, ▼, N₂O; —, Peng–Robinson correlation.

$$f(\delta_{12}) = 100 \left(\frac{\sum |P_{\text{exp}} - P_{\text{calc}}|}{P_{\text{exp}}} \right) / NP \quad (1)$$

where P_{exp} is the experimental bubble point pressure, P_{calc} is the calculated bubble point pressure, and NP is the number of data points. The more complicated objective function used by Weiland et al. (1993) is not necessary as the data cover a limited range of pressures. The data were reasonably well-correlated by the Peng–Robinson equation of state but less accurately than in the system CO₂ + TEGMME. The optimum interaction parameters and objective functions (f) are shown in Table 3.

The data were also correlated by the Krichevsky–Kasarnovsky (1935) equation:

$$\ln(f_2/x_2) = \ln H_{2,1} + (v_2^\infty/RT)(P - P_1^\circ) \quad (2)$$

A plot of $\ln(f_2/x_2)$ versus $P - P_1^\circ$ was prepared and the values of Henry's constants ($H_{2,1}$) were obtained from the intercept of the line with the ordinate. v_2^∞ represents the partial molar volume of the solute at infinite dilution. Values of the fugacity of N₂O were calculated using the Peng–Robinson equation of state with an individual interaction parameter for each data point. The Henry's constants are presented in Table 4. A comparison of the dependence of Henry's constants on the temperature for CO₂ and N₂O is shown in Figure 4.

Figure 3 indicates that the capacity of CO₂ in TEGMME is larger than that of N₂O, in agreement with results for other physical solvents (Laddha et al., 1981; Oyevaar et al., 1989; Xu et al., 1991; Davis et al., 1993). At high

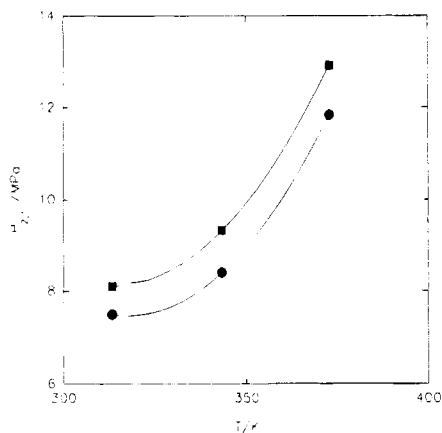


Figure 4. Henry's law constants $H_{2,1}$ for nitrous oxide and carbon dioxide in TEGMME as a function of temperature: ●, CO₂ (Henni and Mather, 1995) ■, N₂O.

pressures the difference in solubility becomes more important. This observation is true for all three temperatures studied. The solubilities of CO₂ and N₂O in TEGMME (Figure 3) are both larger than those in pure water (Müller et al., 1988; Jou et al., 1992; Wiebe et al., 1940). As in the case of water, the ratio of the solubilities of the two gases in the same solvent is practically the same at temperatures of 40, 70, and 100 °C [about 1.09 in TEGMME and 1.41 in water (Jou et al., 1992)]. As previously shown by Xu et al. (1991) and others, this study proves that the value of the N₂O analogy parameter is dependent on the temperature and the properties of solvent.

Conclusions

New experimental data for the solubility of N₂O in TEGMME were obtained at 40, 70, and 100 °C. The results were reasonably well-correlated by the Peng–Robinson equation of state. The Henry's law constants were also derived. At all three temperatures CO₂ is more soluble in TEGMME than N₂O. The N₂O analogy parameters obtained were nearly constant in the temperature range studied and were different from those in water. The data presented in this paper are useful for the theory of gas solubility, the correlation of mixed solvent data, and the removal of N₂O from gas streams.

Registry Numbers Supplied by Author. Triethylene glycol monomethyl ether, 112-35-6.

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